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(54) Title: ELECTRICAL INSULATING OIL BASED COMPOUND AND ITS USE

(57) Abstract

The present invention relates to electrical insulating oil based compounds comprising mineral oils and oil soluble synthetic block-copolymers of polystyrene and synthetic rubber having molecular weights from 50.000-1.000.000. The oil component has preferably a content of aromates of 5-30 weight %. The compounds have high viscosity at low temperatures and are thin liquids at 40-80 °C. The gas absorption capacity of the compounds is high and they are especially useful as insulating compounds in paper wrapped cables, like high voltage DC (HVDC) power cables.

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"ELECTRICAL INSULATING OIL BASED COMPOUND AND ITS USE"

The present invention relates to electrical insulating oil based compounds comprising mineral oils and oil soluble polymers. The compounds are especially useful as electrical insulator in paper wrapped cables, like high voltage DC (HVDC) power cables.

In transformers, starter motors, and other electrical equipment that generate considerable amount of heat, liquids are employed both as insulators and coolants. In cables, capacitors, and connections, insulation liquids are used as a functional component of the dielectric. Organic fluids with low viscosities, in particular mineral oils, are suited for insulating media or dielectrics, for instance, as filling for high-tension transformers, circuit breakers, cables or capacitors. Most liquid insulators consist of mineral oils or synthetic fluids.

Mineral oils, as defined in this application, are complex hydrocarbon mixtures obtained from petroleum oil by fractional distillation and refining. They combine important properties including high breakdown strength, good impregnation characteristics, and the ability to conduct large amounts of heat via convection. Mineral oils can also bind any gas produced during electrical discharge resulting in pronounced evaporation and decomposition. Depending on the predominant hydrocarbon, the oils can be classified as naphtenic or paraffinic based oils, however there is no sharp transition between these groups.

With respect to quantity, the transformer oils represent the major part of the insulating oils. The essential functions of the oil are, beside insulation of the power conductors, to remove the heat generated in the transformer by forced circulation with pumps or by

thermosiphon cooling. In order to achieve a satisfactory heat removal, low-viscosity mineral oils are used world-wide with excellent low-temperature properties.

Switch gear oils are used to protect the contacts of high-voltage circuit breakers against burning due to formation of arcs when the breaker is operated and also to achieve a faster power cut-off. Such oils must possess excellent insulating properties as well as a low viscosity even at low temperatures, in order to allow quick movement of the contact breaker and to fill the gap between the separating contacts.

Underground cables for the transport of medium and high-voltages power contain oil as the insulating medium. Insulation and heating problems can arise, depending on the voltage and power, such that oils with different viscosity grades are needed in cable technology: the higher transmitted voltage, the lower is the required viscosity of the cable oils in order to control heating of the cables, which is the result of ohmic losses in the conductor and of dielectric losses in the insulating material. The oil for the insulation of the voltage-carrying conductor is used to impregnate the multi-layer paper roll which surrounds the conductor. In the cases of high-voltage cables the conductor can be hollow and filled with oil. The oil in the paper roll is in contact with the oil in the hollow conductor via passages, so that the oil can expand into expansion chambers, placed at certain intervals, when the cable becomes hot. If the cable is cooled down, formations of cavities can occur. The formation of cavities in the paper insulation reduces the insulating effect, this in turn leads to gas evolution from the oil due to corona discharge. Both phenomena can create an electrical breakdown hazard.

Such cables, used for the transmission of AC voltages of up to 24 kV, are lapped with paper tapes which are impregnated with a more viscous insulating compound. There is no additional oil feeding system, thus all requirements with respect to insulation stability, particularly the prevention of cavitation, must be satisfied by the impregnating compound. Highly viscous impregnating substances are required in order to prevent migration of the compound from the wrapping resulting in local weakening of the insulation. The compound comprises a highly viscous mineral oil which is further thickened by the addition of natural resins or oil-soluble polymers.

Insulating compounds used in high voltage cables today, contain blends of mineral oils and synthetic homopolymers or refined rosin. The viscosity is high at low temperatures and low at high temperatures, however, the compound becomes a thin liquid first at 100-120^{0}C . When the paper wrapped cables are impregnated, the insulating compound must be a thin liquid.

Accordingly the insulating compound used today must therefore be heated to above 100^{0}C before impregnation, and then cooled down. This cooling step will prolong the production time.

The viscosity profile of the compounds used today does not properly secure that the insulating compound does not leak out of the cable at sub-sea temperatures (below 10°C).

Sparks caused by electrical discharges in gas or vacuum bubbles (cavities) in the insulating material in high voltage cables is a serious problem. The compounds used as insulating material in power cables today does not absorb hydrogen gas to a sufficient degree.

The main object of the present invention was to provide an electrical insulating compound having improved properties and not having the limitations and shortcomings of known electrical insulating compounds.

Another object was to provide a HVDC power cable electrical insulating compound with high viscosity at operating temperatures and a viscosity being suitable for impregnation at temperatures below 100°C. A compound having such a viscosity profile should secure that the impregnation of the paper wrapped cable can be performed at lower temperatures and at a higher rate than presently possible.

A further object of the invention was to provide a compound, which could reduce the risk of the formation of hydrogen gas bubbles or vacuum bubbles, and thereby lower the risk of electrical discharges in the cables.

The inventors carried out a comprehensive study of requirements to be met by the new compound. These studies concluded with the following characteristic properties which the new compound should possess :

a) It should have the ability to absorb hydrogen gas under electrical stress and ionization.

b) It should fulfil the ageing requirements. The dielectric dissipation factor (tgδ at 100°C) should not exceed 0.005 for oil having been exposed to air for 7 days at 125°C.

c) It should have high viscosity at operating temperatures, but should have a steep decrease in viscosity with increasing temperature in order to enable impregnation at temperatures below 100°C. Thus it should be a thin liquid when the paper wrapped cables are impregnated. The insulating compound must penetrate the paper and fill the whole cable, accordingly the viscosity should be low at impregnating temperatures. It is also important that the insulating compound does not leak out during physical damage of the cable. Therefore the viscosity should be high at low temperatures.

d) There should be substantially no asphaltenes in the compound.

e) The total content of sulphur should be below 700 ppm.

f) The compound should not contain sulphur in amounts resulting in corrosion.

Some important properties of the new compound are listed in more detail in table 1.

Table 1

Viscosity	< 300 mPas at t > 80°C >3.000 mPas at t< 20°C
Dissipation factor (tgδ) at 100°C	Newly made compound: < 0.002 After ageing: < 0.005
Dielectric strength (kV/2.5mm)	minimum 30
Gas absorption (mm^3/min)	> -2
Coefficient of expansion/°C	$< 9 \times 10^{-4}$

When the inventors were looking for a compound which would fulfil all the above mentioned requirements, they found that by blending together mineral oils and synthetic block-copolymers, particularly polystyrene rubber, they would end up with useful compounds. These results lead to a comprehensive study of such mixtures. The conclusion drawn from these studies was that the following components would be applicable within the following definition :

Oil : Mineral oils. The oil should be predominantly naphtenic with relatively high content of aromates.

Polymer : Oil soluble, synthetic hydrocarbonic block-copolymer of polystyrene and synthetic rubber, having molecular weight from 50.000- 1.000.000. The rubber part should be ethylene-/buthylene-, isoprene- or butadiene rubber.

Sometimes it can be useful to add a compound which increase the gas absorption, i.e. alkylbenzene, like dodecylbenzene, dialkylbenzenes or diarylalkanes, to the mixture of oils and block-copolymers. Further, polyisobutylene can be added to increase the viscosity of the compound.

The ratio between the oils and the polymer was found to be of importance. Further it was found that it would be advantageous to apply different types of oils, for instance :

Oil 1	:	Mineral oil with 10-30 weight% aromatic hydrocarbons. Viscosity : 5 - 10 mPas/°C at 25°C Boiling point : > 300°C
Oil 2		Hydrogenated, naphtenic mineral oil. Viscosity: 5 - 10 mPas/°C at 25°C. Boiling point : > 250°C
Oil 3	:	Hydrogenated, naphtenic mineral oil. Viscosity : 90 - 100 mPas/°C at 25°C. Boiling point : > 300°C

The content of aromates in the oil component of the compound should preferably be 5-30 weight%.

The performed study revealed that the composition of the electrical insulating compound according to the invention should be within the following ranges :

Polymer	:	3 - 10 % (weight/total weight)
Oil 1	:	10 - 90 % (weight/total weight)
Oil 2	:	0 - 15 % (weight/total weight)
Oil 3	:	0 - 85 % (weight/total weight)

The most suitable compositions for HVDC power cables were found to have the following compositions.

3 - 10 % (weight/total weight) of a styrene-ethylene/buthylene-styrene tri-block and the oil component comprises:
60 - 80 % (weight/total weight) of an mineral oil with 10-30 % aromatic hydrocarbons, 7 - 15 % (weight/total weight) of a hydrogenated, naphtenic mineral oil having boiling point >250°C and 7 - 15 % (weight/total weight) of a hydrogenated, naphtenic mineral oil having boiling point >300°C.

or

3-10 % (weight/total weight) of a styrene-isoprene-styrene tri-block
60-70 % (weight/total weight) of an mineral oil with 10-30 % aromatic hydrocarbons and 20-30% (weight/total weight) of dodecylbenzene.

or

5.0-6.0 % (weight/total weight) of a styrene-ethylene/buthylene-styrene tri-block
45-75 % (weight/total weight) of an mineral oil with 10-30 % aromatic hydrocarbons and 20-50 % (weight/total weight) of a hydrogenated, naphtenic mineral oil.

or

3.0-10 % (weight/totaal weight) synthetic hydrocarbon block-copolymer, 10-15 % (weight/total weight) of an mineral oil with 10-30% aromatic hydrocarbons and 75-85 % (weight/total weight) of a hydrogenated, naphtenic mineral oil having boiling point >300°C.

Further it is preferred that the block-copolymer is a styrene-ethylene/buthylene-styrene tri-block or styrene-isoprene-styrene tri-block.

When the properties of the insulating oils were measured, the following methods were used

Viscosity	:	Instrument	:	Bohlin VOR Rheometer
		Conditions	:	Measuring system, C 25
		Temperature	:	80 - 4°C, 0.2-0.5°C/min
		Shear Rate	:	0.581 s^{-1}

Gas absorption: Gassing of insulating liquids under electric stress and ionisation (IEC Standard Publication 628)

Dielectric dissipation factor (tg δ) or dielectric loss : Method : IEC 247.

Expansion coefficient (α) :Thermal volumetric expansion coefficient pro degree Kelvin (K^{-1}).

$$V = V_o(1+ \alpha t).$$

The scope and special features of the invention are as defined in the attached claims.

The invention will now be further explained in connection with the description of the figures and the examples.

Figs. 1 - 5 shows the viscosity profiles, viscosity as function of temperature, of the insulating compounds prepared in examples 1 - 4 compared with a known insulating compound. Curve I on the figures refers to the known compound and curve II to the exemplified compounds according to the invention.

Example 1

This example shows preparation of an electrical insulating oil based compound according to the invention. In figure 1, curve II is the viscosity profile of the compound shown. The known compound (Curve I) which the new compounds are compared with, is a commercially available insulating compound based on viscous mineral oil thickened by addition of oil-soluble polymers.

Recipe: 6.00 % (weight/total weight) of a styrene-ethylene/buthylene-styrene tri-block
70.50 % (weight/total weight) of oil 1
11.75 % (weight/total weight) of oil 2
11.75 % (weight/total weight) of oil 3

The oil components and the block copolymer are mixed in a reactor until the particles are evenly distributed. Then the reactor is heated to 80-120°C and when all the copolymer are dissolved the mixture is evacuated and the temperature is reduced to about 70°C. The mixture is subsequently filtered, preferably with diatomaceous earth.

The filtered compound had the following properties:

Dissipating factor (tgδ) at 100°C	:	New compound :	0.0020
		After ageing :	0.0027
Dielectric strength (kV/2.5 mm)	:	>60	
Gas absorption (mm^3/min)	:	-10.8	
Specific gravity at 20°C (g/ml)	:	0.85	
Coefficient of expansion K^{-1}	:	0.000676	

Example 2

This example shows preparation of an electrical insulating oil based compound containing an alkyl benzene, which secure high gas absorption. In figure 2, curve II, shows the viscosity profile of the compound.

Recipe : 10 % (weight/total weight) of a styrene-isoprene-styrene tri-block
65 % (weight/total weight) of oil 1
25 % (weight/total weight) of dodecylbenzene

The electrical insulating compound was prepared in the same way as the compound in example 1.

The compound has the following properties :

Dissipating factor (tgδ) at 100°C	:	New compound	0.041
-"-		After ageing	0.045
Dielectric strength (kV/2.5 mm)	:	36-46	
Gas absorption (mm^3/min)	:	-15	
Coefficient of expansion K^{-1}	:	0.00068	
Specific gravity at 20°C (g/ml)	:	0.85	

Example 3

This example shows the composition of some further electrical insulating compounds according to the invention. Their gas absorption properties are stated and their viscosity profile are shown in figure 3, curve II for recipe A and figure 4, curve II for recipe B.

Recipes :

A) 5.0% (weight/total weight) of a styrene-ethylene/buthylene-styrene tri-block
47.5% (weight/total weight) of oil 1
47.5% (weight/total weight) of oil 2

B) 6.0% (weight/total weight) of a styrene-ethylene/buthylene-styrene tri-block
70.5% (weight/total weight) of oil 1
23.5% (weight/total weight) of oil 2

The compounds had the following properties :		A	B
Dissipating factor (tgδ) at 100°C:	New compound	0.0020	0.0020
	After ageing	0.0030	0.0030
Dielectric strength (kV/2.5 mm) :		>40	>40
Gas absorption (mm^3/min)		-2.0	-8.0
Coefficient of expansion K^{-1}		0.0007	0.007
Specific gravity at 20°C (g/ml)		0.85	0.85

Example 4

This example shows preparation of an insulating oil based compound having a high content of hydrogenated naphtenic mineral oil and a viscosity < 3.0 Pas at 60°C. The viscosity profile for the compound is shown in figure 5, curve II.

Recipe: 9.00 % (weight/total weight) of a styrene-ethylene/buthylene-styrene tri-block
11.00 % (weight/total/weight) of oil 1
83.00 % (weight/total weight) of oil 3

The insulating compound was prepared as the compound of example 1.

The compound had the following properties :

Dissipating factor (tgδ) at 100°C:	New compound	0.0020
	After ageing	0.0030
Dielectric strength (kV/2.5 mm) :		>40
Gas absorption (mm^3/min) :		-7.5
Coefficient of expansion K^{-1}		0.00069
Specific gravity at 20°C (g/ml) :		0.85

The results of the above examples show that the inventors have succeeded in arriving at an electrical insulating compound with good gas absorption capacities and viscosity profiles which will fulfil all the requirements mentioned above. The electrical insulating compound will absorb gas in such a way that the formation of gas bubbles (cavities) is prevented. Since the formation of cavities are prevented, there will be no sparks caused by electrical discharges, accordingly creation of electrical breakdown hazard or alteration of the dielectric will be prevented. The new insulating compound is more resistant to ageing.

The figures 1-4 shows that the viscosity is below 200 mPas at the 80°C. These insulating compounds have low viscosity at 40-80°C. This secure good impregnation of the paper wrapped cables. Since the insulating compounds can be thin liquids already at 40°C, the

production can be performed at a much higher rate than what was possible previously. The figures also shows that the viscosity to the new electrical insulating compounds are much higher below 20°C than the viscosity for the old electrical insulating compound. This give an even higher security against leakage out of the cable of the electrical insulating compound if the cable is physically damaged. In some cases a steep viscosity profile is required. This is achieved by adjusting the composition of the compound and still fulfil the other requirements. Example 4 and figure 5 show such a compound and its viscosity profile.

The new electrical insulating compounds are especially suitable for application in high voltage DC power cables as shown by the above examples. However, the compounds can also be used for other insulating purposes being obvious in view of the properties of the compounds.

Claims

1. Oil based electrical insulating compound comprising mineral oils and an oil soluble polymer being a synthetic hydrocarbonic block-copolymer of polystyrene and synthetic rubber having molecular weights from 50.000-1.000.000.

2. Oil based compound according to claim 1,
c a r a c t e r i z e d i n t h a t
the mineral oils have a content of aromates of 5-30 weight%.

3 Oil based compound according to claim 4,
c a r a c t e r i z e d i n t h a t
the rubber component of the block-copolymer is styrene-ethylene/buthylene-styrene tri-block or styrene-isoprene-styrene tri-block.

4. Oil based compound according to claim 1,
c a r a c t e r i z e d i n t h a t
the oil based compound comprises a compound which increase the gas absorption capacity.

5. Oil based compound according to claim 2.
c a r a c t e r i z e d i n t h a t
the compound which increase the gas absorption capacity is dodecylbenzene. diarylalkanes dialkylbenzenes or alkylbenzenes.

6 Oil based compound according to claim 1,

c a r a c t e r i z e d i n t h a t

the compound contains :

3 - 10 % (weight/total weight) of a styrene-ethylene/buthylene-styrene tri-block and the oil component comprises :

60 - 80 % (weight/total weight) of an mineral oil with 10-30 % aromatic hydrocarbons 7 - 15 % (weight/total weight) of a hydrogenated, naphtenic mineral oil having boiling point >250°C and 7 - 15 % (weight/total weight) of a hydrogenated, naphtenic mineral oil having boiling point >300°C.

7. Oil based compound according to claim 1,

c a r a c t e r i z e d i n t h a t

the compound contains :

3-10 % (weight/total weight) of a styrene-ethylene/buthylene-styrene tri-block and the oil component comprises :

10-15 % (weight/total weight) of an mineral oil with 10-30 % aromatic hydrocarbons, 75-85 % (weight/total weight) of a hydrogenated, naphtenic mineral oil having boiling point >300°C.

8. Oil based compound according to claim 1,

c a r a c t e r i z e d i n t h a t

the compound contains :

3-10% (weight/total weight) of a styrene-isoprene-styrene tri-block

60-70% (weight/total weight) of an mineral oil with 10-30 % aromatic and

20-30% (weight/total weight) of dodecylbenzene.

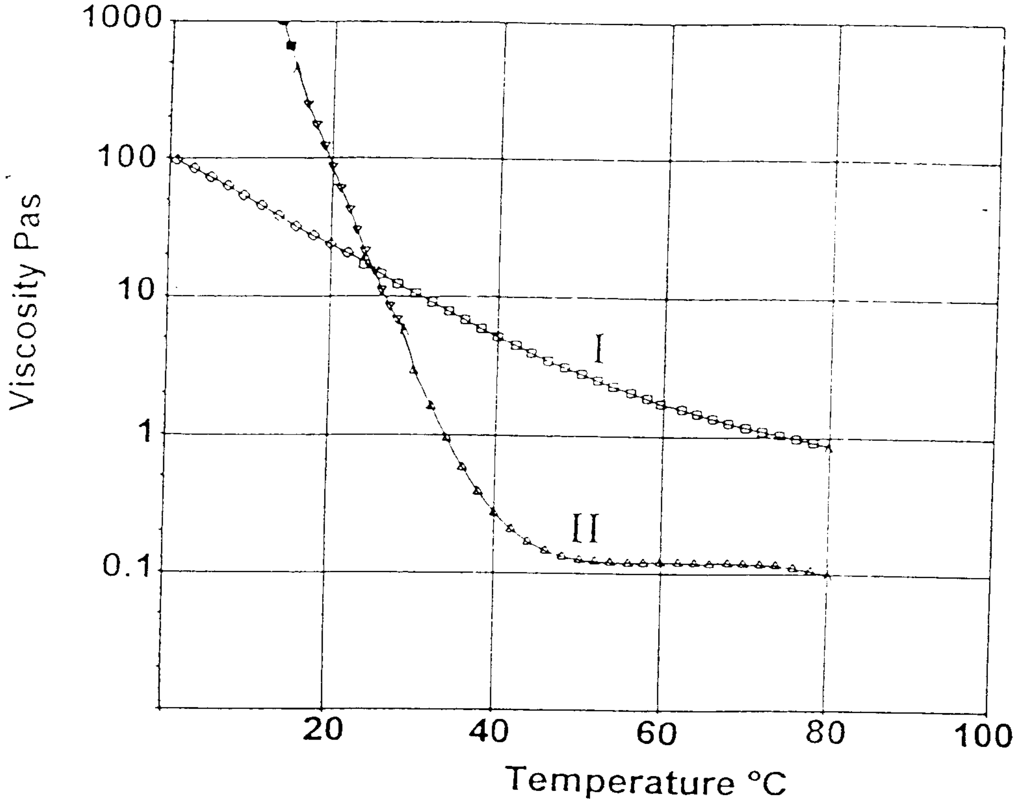
9. Oil based compound according to claim 1,

c a r a c t e r i z e d i n t h a t

the compound contains :

5.0-6.0% (weight/total weight) of a styrene-ethylene/buthylene-styrene tri-block 45-75% (weight/total weight) of an mineral oil with 10-30 % aromatic hydrocarbons and 20-50 % (weight/total weight) of a hydrogenated, naphtenic mineral oil.

10. Use of the oil based compound according to claims 1-9 as an electrical insulating and filling compound in high voltages DC power cables.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Viscosity Pas
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60
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100
Temperature °C
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II

Fig. 1

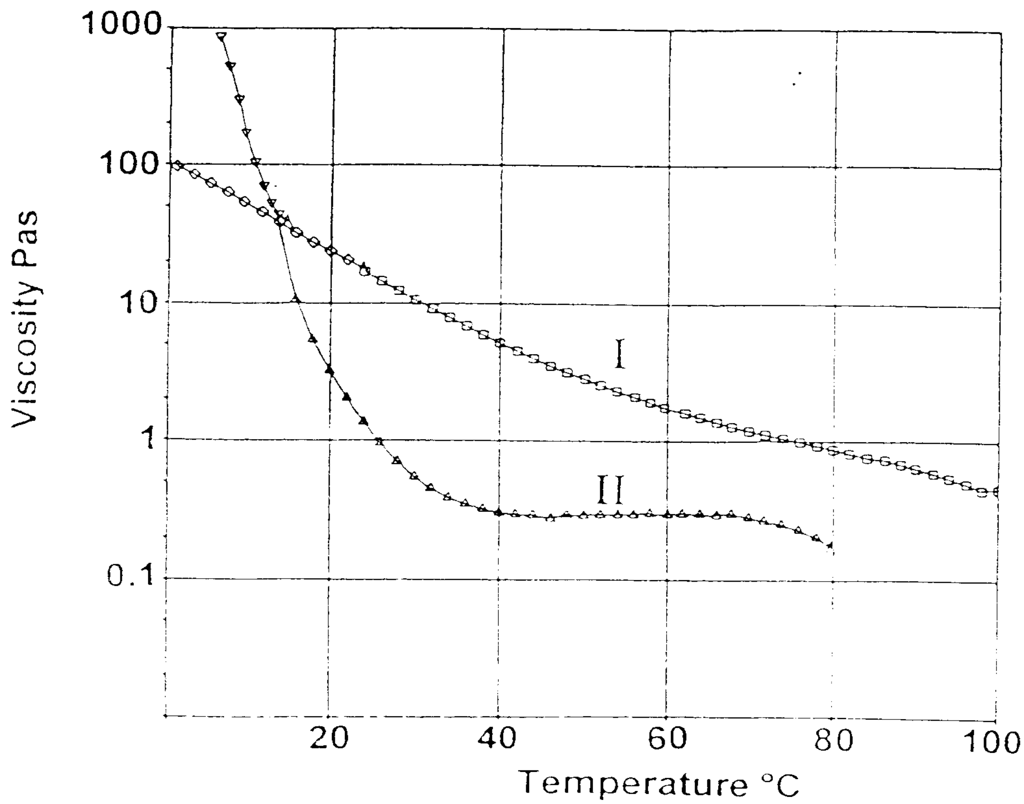
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Fig. 2

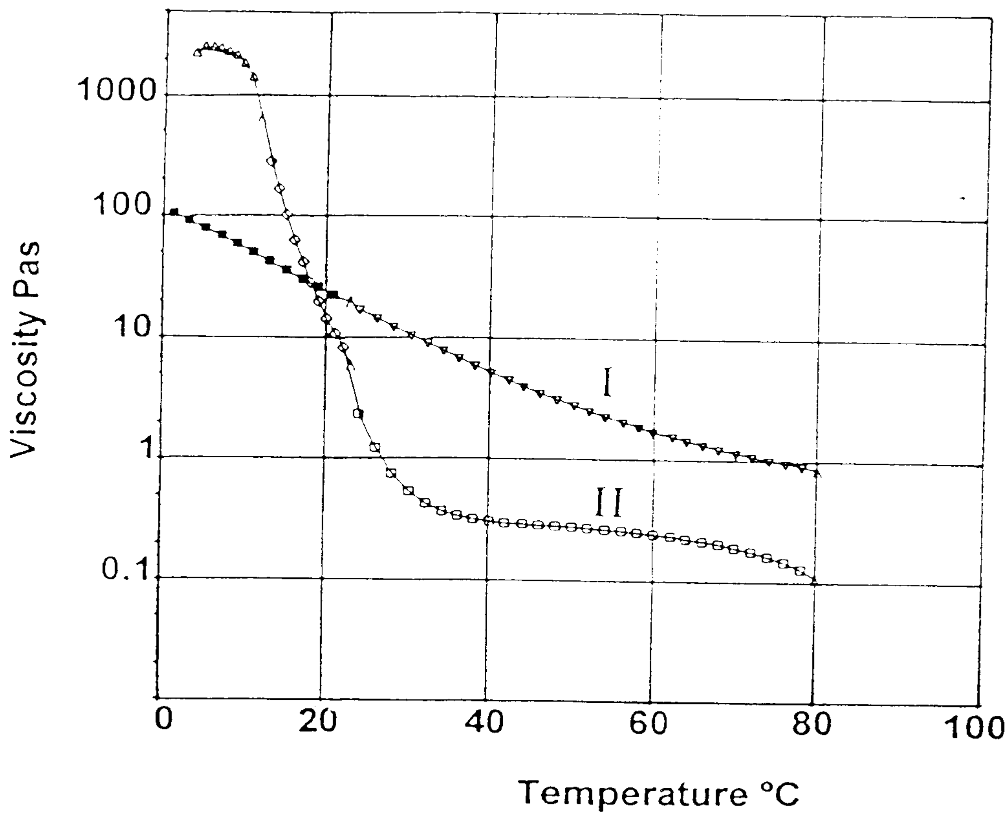
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Fig. 3

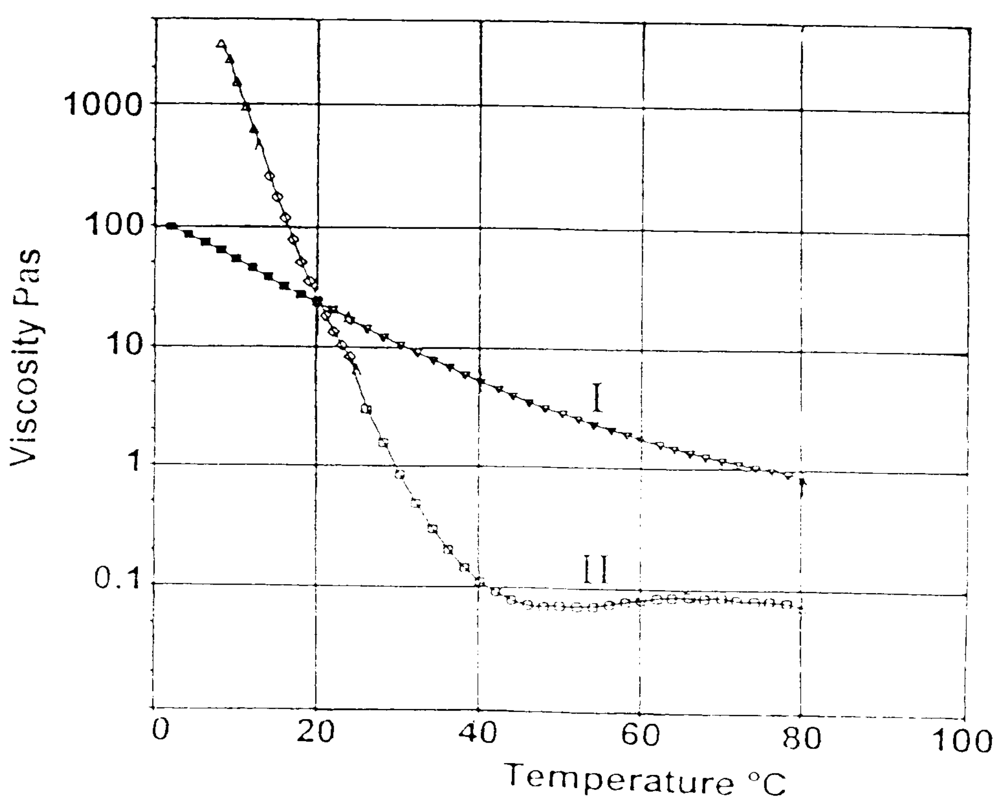
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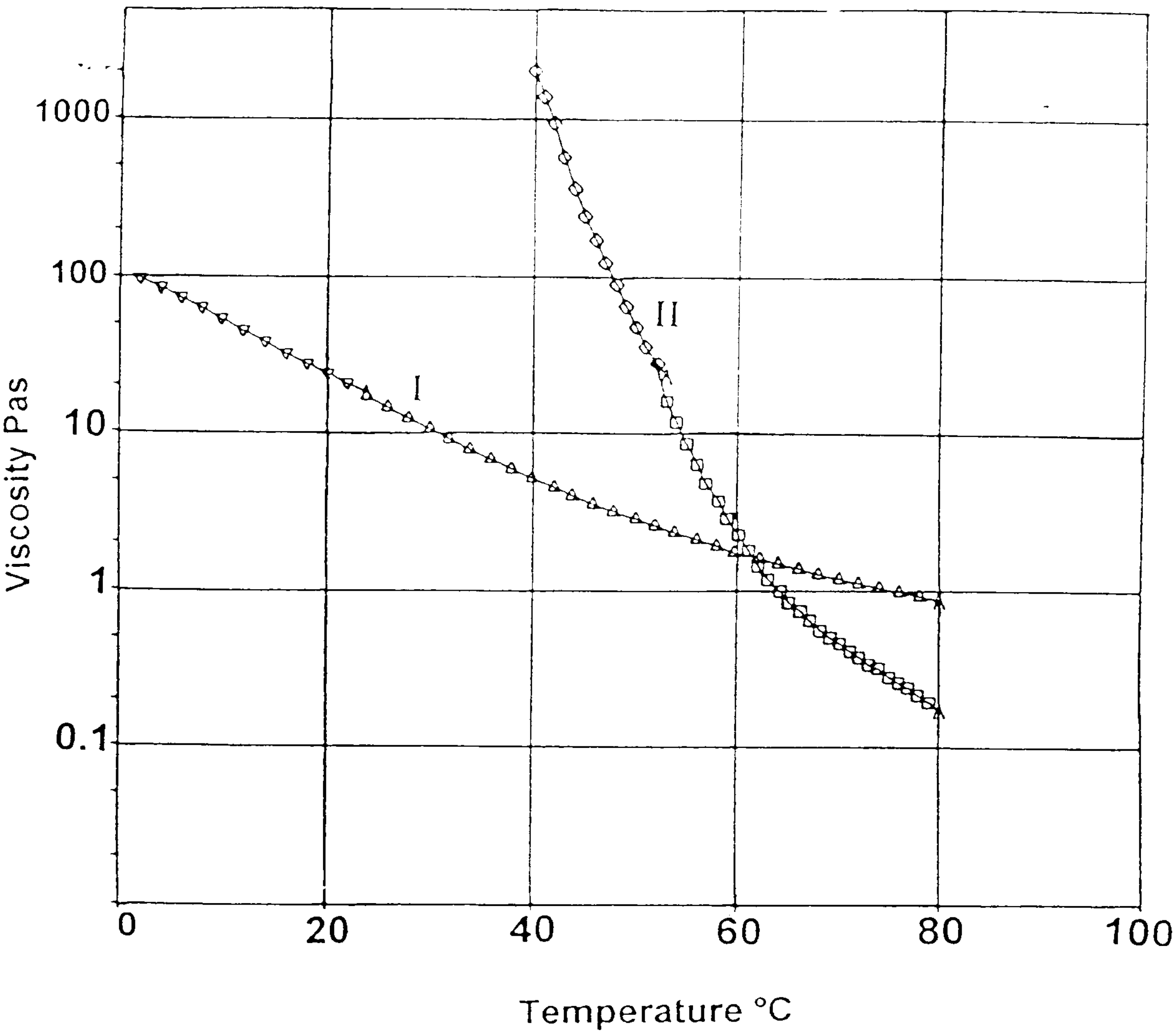
Fig. 4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Viscosity Pas
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60
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Temperature °C

Fig. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 96/00172

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: H01B 3/20, H01B 3/22, H01B 3/28
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4351913 A (NAREN I. PATEL), 28 Sept 1982 (28.09.82), column 4, line 8 - line 47, claim 1, abstract --	1-10
X	EP 0231402 A1 (SHELL OIL COMPANY ET AL), 12 August 1987 (12.08.87), claims 1-6, abstract --	1-10
A	US 3879575 A (DONALD PATRICK DOBBIN ET AL), 22 April 1975 (22.04.75) -- --------	1-10

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
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Date of the actual completion of the international search	Date of mailing of the international search report
14 October 1996	18 -10- 1996

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INTERNATIONAL SEARCH REPORT
Information on patent family members

01/10/96

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PCT/NO 96/00172

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